

CLAIMS

1. A thermoset plastic material, comprising a three-dimensional matrix containing sulphur atoms and at least one antiplasticizing additive
 5 that does not react with said matrix.

2. A thermoset plastic material according to claim 1, wherein the three-dimensional matrix is a polythiourethane matrix or a polyepisulfide matrix.

3. A material according to claim 1 or 2, wherein antiplasticization
 10 occurs in the range of temperatures from 0 to 85°C.

4. A material according to any one of preceding claims, wherein the antiplasticizing additive has a solubility parameter δ_a satisfying the following relation:

$$\delta_{mo} - \delta_a < 5 \text{ MPa}^{1/2}$$

15

wherein δ_{mo} corresponds to the solubility parameter of the polyisocyanate and polythiol monomers used to produce the polythiourethane matrix.

5. A Material according to any one of preceding claims, wherein
 20 the solubility parameter δ_a of the antiplasticizing additive does satisfy the following relation:

$$\delta_{ma} - \delta_a > 4 \text{ MPa}^{1/2}$$

25

wherein δ_{ma} corresponds to the solubility parameter of the matrix.

6. A material according to any one of preceding claims, wherein the solubility parameter of the plasticizing additive does satisfy the following relation:

$$19 \leq \delta_a \leq 23.$$

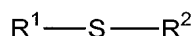
30

7. A material according to any one of preceding claims, wherein the antiplasticizing additive is selected from dialkyl sulfides, diaryl sulfides, dialkylaryl sulfides, alkylaryl sulfides, aryl and alkylaryl sulfides, aryl and alkyl silane sulfides, carbonyl derivatives, S-arylthioalkylates, bis-

arylthioalkyls, thiourea derivatives, urethane derivatives, diurethane derivatives and mixtures thereof.

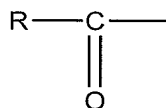
8. A material according to claim 7, wherein the sulfides have following formula:

5



wherein R^1 and R^2 , being the same or different, represent independently from each other an alkyl radical, preferably a C_1 - C_{12} alkyl radical, more preferably a C_4 - C_{10} alkyl radical and in particular an octyl radical; a cycloalkyl radical, preferably a 6-membered radical, such as a cyclohexyl radical; an aryl radical such as a phenyl radical; an arylalkyl radical such as a benzyl radical; a radical

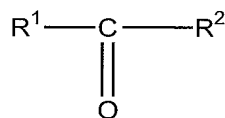
15



wherein R is an alkyl radical, preferably a C_1 - C_6 alkyl radical, such as a methyl, ethyl, propyl radical; a trialkyl silane radical, especially a trimethyl silane.

20

9. A material according to claim 7, wherein carbonyl derivatives have following formula:

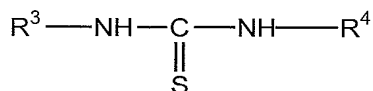


25

wherein R^1 and R^2 are such as defined in claim 7.

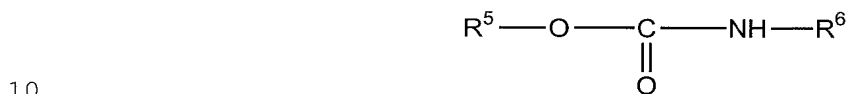
10. A material according to claim 7, wherein thiourea derivatives have following formula:

30



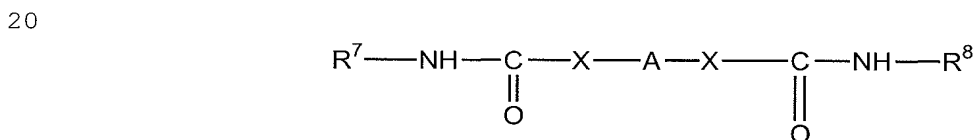
wherein R^3 and R^4 , being the same or different, represent independently from each other an alkyl radical, preferably a C_1 - C_{12} alkyl radical, more preferably a C_4 - C_{10} alkyl radical, a cycloalkyl radical, preferably a 6-membered radical such as a cyclohexyl radical; an alkyl radical bearing a nitrogen and/or an oxygen heterocycle such as a 4-morpholinoalkyl radical, especially a 4-morpholinoethyl radical.

11. A material according to claim 7, wherein urethane derivatives have following formula:



wherein R^5 and R^6 , being the same or different, represent independently from each other a cycloalkyl group, preferably a 6-membered radical, such as a cyclohexyl radical; a cycloalkyl alkyl group such as a cyclohexylalkyl group, in particular a cyclohexylpropyl group; an aryl group such as a phenyl group; an arylalkyl group in particular a phenylpropyl group.

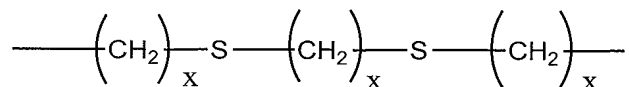
12. A material according to claim 7, wherein the thiourethane derivatives have following formula:



wherein A represents a C_1 - C_{12} alkylene group, preferably a C_6 - C_{10} alkylene group, in particular an octylene group, a group:



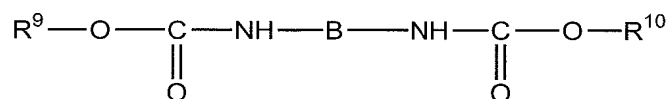
or:



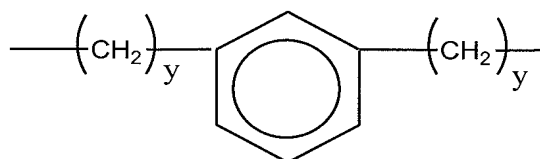
wherein x is an integer ranging from 1 to 6, preferably x is 2; X represents -O- or -S-; and R^7 and R^8 represent independently from each

other, a cycloalkyl group, preferably a 6-membered group, in particular a cyclohexyl group, or an aryl group, preferably a 6-membered group, in particular a phenyl group.

13. A material according to claim 7, wherein diurethane derivatives
5 have the following formula:

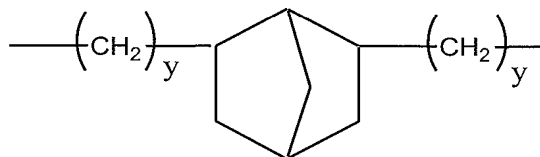


wherein B represents a radical of formula:

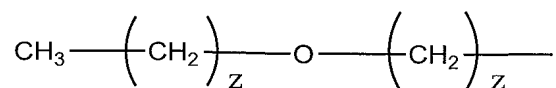


10

or



15 wherein y is an integer ranging from 1 to 4, preferably y is 1, and
R⁹ and R¹⁰ represent independently from each other, a cycloalkyl alkyl
radical, in particular a cyclohexyl (C₁-C₆)alkyl radical such as a
cyclohexylethyl or a cyclohexylpropyl radical; an aryl (C₁-C₆)alkyl
radical, in particular a phenylpropyl radical; a (bridged) cycloalkyl (C₁-
20 C₆)alkyl radical such as a norbornylmethyl radical; ether-oxide radicals of
formula:

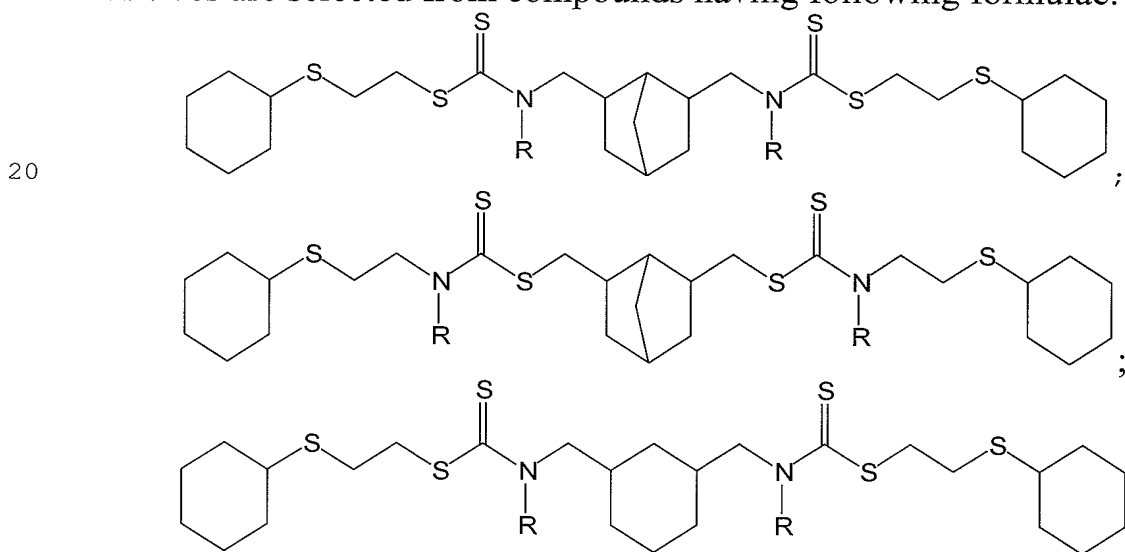


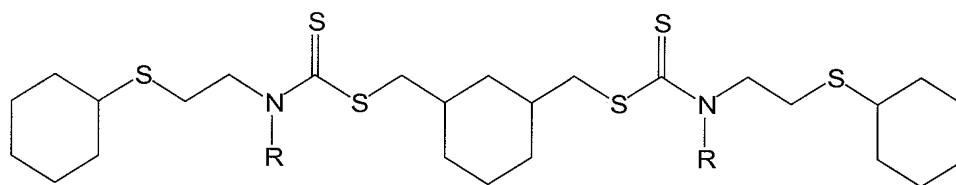
25 wherein z is an integer ranging from 1 to 4, preferably z is 2.

14. A material according to claim 7, wherein the antiplasticizing
additives are selected from dioctyl sulfide, benzyl and phenyl sulfide,

dibenzyl sulfide, 4-(p-tolylthio)benzophenone, bis(phenylthio)methane, S-phenylthiopropionate, phenylthiomethyltrimethyl silane, 1-cyclohexyl-3-(2-morpholinoethyl)-2-thiourea, cyclohexylpropylcyclohexyl urethane, phenylpropylcyclohexyl-(octane diurethane), cyclohexylpropyl-
 5 cyclohexylpropylxylylene diurethane, cyclohexylethyl-cyclohexylethylxylylene diurethane, phenylpropyl-phenylmethane, propoxyethyl-propoxyethylxylylene diurethane, norbornanemethyl-norbornanemethylxylylene diurethane, phenylpropyl-phenylpropylxylylene diurethane, cyclohexyl-cyclohexyl (thiodiethane
 10 di-S-thiourethane), phenyl-phenyl (thiodiethane di-S-thiourethane), cyclohexyl-cyclohexyl (dithiaoctane diurethane), cyclohexylpropyl-cyclohexylpropyl dimethyl norbornane diurethane, cyclohexylethyl-cyclohexylethyldimethyl norbornane diurethane, propoxyethyl-propoxyethyldimethyl norbornane diurethane, norbornanemethyl-
 15 norbornanemethyldimethyl norbornane diurethane, phenylpropyl-phenylpropyl-dimethyl norbornane diurethane, cyclohexyl-cyclohexyl (thiodiethane diurethane), phenyl-phenyl (thiodiethane diurethane).

15. A material according to claim 7, wherein the antiplasticizing additives are selected from compounds having following formulae:





wherein R represents H, an alkyl group, especially, a methyl, ethyl, n-propyl or n-butyl group, or an aryl group, especially a phenyl group.

16. A material according to any one of preceding claims, wherein the antiplasticizing additive is present in amount ranging from 5 to 25%, preferably from 5 to 15%, by weight as compared to the total weight of the polythiourethane matrix.

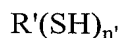
17. A material according to any one of preceding claims, wherein the polythiourethane matrix is produced by polyaddition of at least one polyisocyanate, preferably a diisocyanate and at least one polythiol, preferably a tri- or tetrathiol.

18. A material according to claim 17, wherein the polyisocyanate is selected from aromatic polyisocyanates, aliphatic polyisocyanates, cycloaliphatic polyisocyanates and mixtures thereof.

19. A material according to claim 18, wherein the polyisocyanate is selected from phenylene diisocyanate, ethylphenylene diisocyanate, isopropylphenylene diisocyanate, dimethylphenylene diisocyanate, diethylphenylene diisocyanate, diisopropylphenylene diisocyanate, trimethylbenzyl triisocyanate, xylylene diisocyanate (XDI), benzyl triisocyanate, 4,4'-diphenylmethanediisocyanate and isophorone diisocyanate, hexamethylene diisocyanate, bis(isocyanate)methyl cyclohexane, dicyclohexyl methane diisocyanate, dimethyl norbornyl diisocyanate (NDI) and norbornyl methyl diisocyanate, and mixtures thereof.

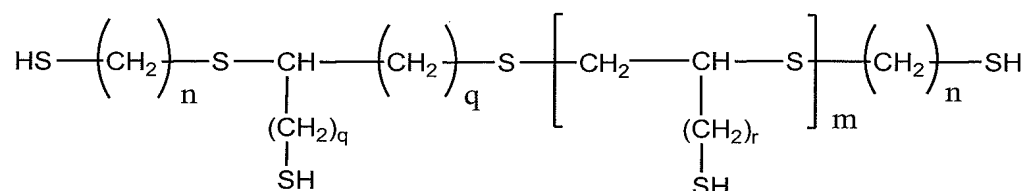
20. A material according to claim 19, wherein the polyisocyanate is selected from xylylene diisocyanate, dimethyl norbornyl diisocyanate and mixtures thereof.

21. A material according to any one of preceding claims, wherein the polythiol has following formula:



wherein R' represents an organic group the valence of which corresponds to n'; where n' is an integer ranging from 2 to 6, preferably n is 3 or 4.

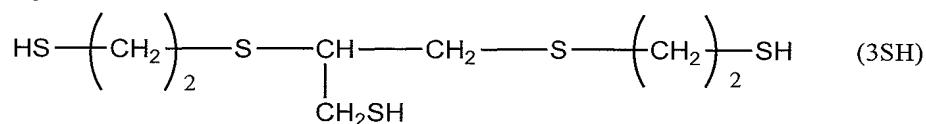
22. A material according to claim 21, wherein the polythiol has following formula:



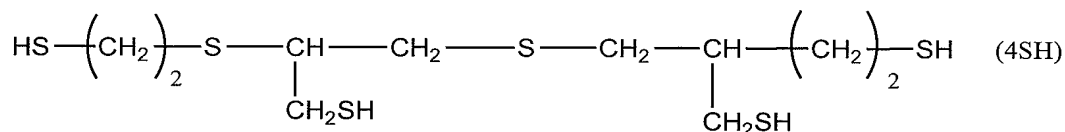
wherein n is an integer ranging from 1 to 4, preferably n is 2, p, q and r are integers ranging from 1 to 4, preferably p, q and r are 1, and m is the integer 1 or 2.

23. A material according to claim 22, wherein the polythiol is selected from pentaerythritol tetrakis mercaptopropionate, 1-(1'-mercaptoethylthio)-2,3-dimercapto propane, 1-(2'-mercaptopropylthio)-2,3-dimercapto propane, 1-(3'-mercaptopropylthio)-2,3-dimercapto propane, 1-(4'-mercaptobutylthio)-2,3-dimercapto propane, 1-(5'-mercaptopentylthio)-2,3-dimercapto propane, 1-(6'-mercaptohexylthio)-2,3-dimercapto propane, 1,2-bis(4'-mercaptobutylthio)-3,mercapto propane, 1,2-bis(6'-mercaptohexyl)-3-mercapto propane, 1,2,3-tris(mercaptomethylthio)propane, 1,2,3-tris(3'-mercaptopropylthio)propane, 1,2,3-tris(2'-mercaptoethylthio)propane, 1,2,3-tris-(4'-mercaptobutylthio)propane, 1,2,3-tris(6'-mercaptohexylthio)propane, 1,6-hexanethiol-1,2,3-propanetritiol and 1,2-bis(2'-mercaptoethylthio)-3-mercapto propane.

24. A material according to claim 23, wherein the polythiol has following formula:



or



25. A material according to any one of claims 2 to 17, wherein the polythiourethane matrix is produced by means of a polyaddition reaction of a NCO end group-containing polythiourethane prepolymer with a SH end group-containing polythiourethane prepolymer.

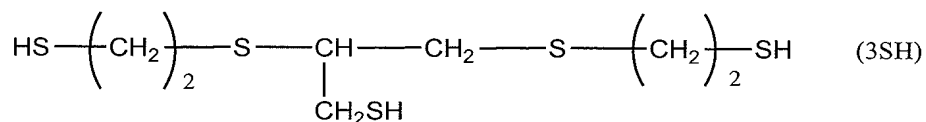
26. A material according to claim 22, wherein the NCO end group-containing polythiourethane prepolymer has a number average molecular weight ranging from 1000 to 2000, preferably ranging from 1300 to 1700.

27. A material according to claim 25 or 26, wherein the NCO end group-containing polythiourethane prepolymer has a NCO/SH ratio from 4:1 to 30:1, preferably of 6:1 or more, and more preferably of about 8:1.

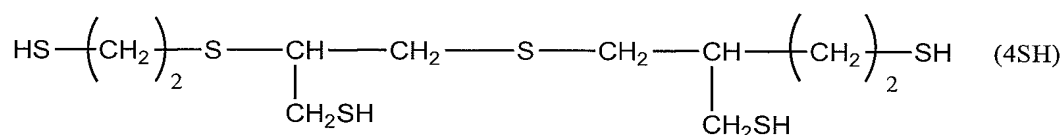
28. A material according to any one of claims 25 to 27, wherein the SH end group-containing polythiourethane prepolymer has a number average molecular weight ranging from 200 to 300.

29. A material according to any one of claims 25 to 28, wherein the SH end group-containing polythiourethane prepolymer has a SH/NCO ratio ranging from 4:1 to 30:1, preferably of 6:1 or more, and more preferably of 8:1.

30. A material according to any one of claims 25 to 29, wherein the NCO end group-containing polythiourethane prepolymer and/or the SH end group-containing polythiourethane prepolymer results from the polyaddition of xylene diisocyanate and/or dimethyl norbornyl diisocyanate with polythiol of formula:



and/or



31. A thermoset material according to any one of preceding claims having a phase separation, preferably a nanophase separation.

32. A thermoset material according to any one of preceding claims having an energy release ratio G_{IC} of at least 0.15 kJ.m^{-2} , more preferably of at least 0.20 kJ.m^{-2} .

33. An ophthalmic lens comprising an optically transparent, thermoset plastic material, comprising a three-dimensional polymer matrix, the loss modulus (E'') of which presenting a secondary glass transition (β), and at least one antiplasticizing additive.

34. An ophthalmic lens according to claim 33, wherein the thermoset material presents a nanophase separation.

35. An ophthalmic lens according to claim 33 or 34, wherein the matrix is selected from a polyurethane matrix or a matrix produced by polymerizing a composition comprising at least one polyepisulfide.

36. An ophthalmic lens according to any one of claims 33 to 35, wherein the antiplasticizing additive has a solubility parameter δ_a that does satisfy following relation:

$$\delta_{mo} - \delta_a < 5 \text{ MPa}^{1/2}$$

wherein δ_{mo} corresponds to the solubility parameter of the polyisocyanate and polythiol monomers used to produce the polythiourethane matrix.

37. An ophthalmic lens according to any one of claims 33 to 36, wherein the solubility parameter δ_a of the antiplasticizing additive does satisfy the following relation:

$$\delta_{ma} - \delta_a > 4 \text{ MPa}^{1/2}$$

wherein δ_{ma} corresponds to the solubility parameter of the matrix.

38. An ophthalmic lens according to claim 33, wherein the thermoset material is such as defined in anyone of claims 1 to 32.